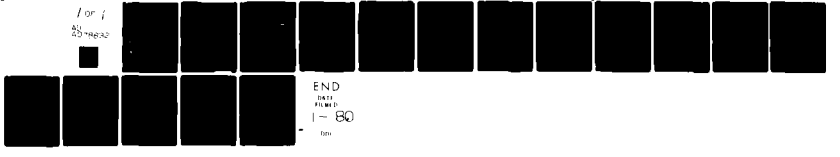
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Long-Term Thermal Stability of Solithane, a Candidate TWT Encapsulant

Prepared by

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30 September 1979

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Final Report
1 February to 30 September 1978

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Prepared for

SPACE AND MISSILE SYSTEMS ORGANIZATION
AIR FORCE SYSTEMS COMMAND
Los Angeles Air Force Station
P.O. Box 92960, Worldway Postal Center
Los Angeles, Calif. 90009

80- 4 1 017

This final report was submitted by The Aerospace Corporation, El Segundo, CA 90245, under contract F04701-78-C-0079 with the Space and Missile Systems Organization, Deputy for Space Communications Systems, P.O. Box 92960, Worldway Postal Center, Los Angeles, CA 90009. It was reviewed and approved for The Aerospace Corporation by H. E. McDonnell, Programs Group. Major C. J. Kennedy, SAMSO/SKX was the project engineer.

This report has been reviewed by the Office of Information and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nationals.

This technical report has been reviewed and is approved for publication.

Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

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SECURITY CLASSIFICATION OF THIS PAGE *(When Data Entered)*

REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER: SAMSO-79-038	2. GOVT ACCESSION NO. / 3. RECIPIENT'S CATALOG NUMBER
4. TITLE *(and Subtitle)*: LONG-TERM THERMAL STABILITY OF SOLITHANE, A CANDIDATE TWT ENCAPSULANT	5. TYPE OF REPORT & PERIOD COVERED: Final rept. 1 Feb – 30 Sept [illegible]78
	6. PERFORMING ORG. REPORT NUMBER: TR-0079(4402)-1
7. AUTHOR(s): Camille A. Gaulin, Vester L. Knight and Manfred Buechler	8. CONTRACT OR GRANT NUMBER(s): F04701-78-C-0079
9. PERFORMING ORGANIZATION NAME AND ADDRESS: The Aerospace Corporation, El Segundo, California 90245	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS: Space and Missile Systems Organization, Air Force Systems Command, Los Angeles Air Force Station, P. O. Box 92960, Worldway Postal Center, Los Angeles, California 90009	12. REPORT DATE: 30 Sept [illegible]79 13. NUMBER OF PAGES: 13
	15. SECURITY CLASS. *(of this report)*: Unclassified
14. MONITORING AGENCY NAME & ADDRESS *(if different from Controlling Office)*	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT *(of this Report)*

Approved for public release; distribution unlimited.

12 17

17. DISTRIBUTION STATEMENT *(of the abstract entered in Block 20, if different from Report)*

18. SUPPLEMENTARY NOTES

19. KEY WORDS *(Continue on reverse side if necessary and identify by block number)*

Encapsulant	Collector
Polyurethane	Thermogravimetric Analysis (TGA)
Solithane 113	Mass Spectrometry
Traveling-Wave Tube (TWT)	Thermal Degradation

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

In support of traveling-wave tube amplifier tube encapsulant evaluations, a cured sample of Solithane 113 (a polyurethane potting compound supplied by Watkins-Johnson) was exposed to a vacuum-thermal (120°C) environment for 300+ hours to determine if chemical degradation occurs on such exposure. Degradation was determined qualitatively by sampling into a quadrupole mass spectrometer the gases and vapors produced from the sample and analyzing the spectra of the gases. The resultant spectra indicated

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SECURITY CLASSIFICATION OF THIS PAGE *(When Data Entered)*

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19. KEY WORDS (Continued)

20. ABSTRACT (Continued)

significant thermochemical degradation of the polymer under the conditions of the exposure. These results should be factored into deliberations on the choice of encapsulants for TWTA components. Degradation of this kind may markedly affect physical-chemical properties of the material over the long term and should be treated as a potential source of tube failure due to corona discharge.

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I. INTRODUCTION

The Watkins-Johnson Company (W-J)* is involved in the development of traveling-wave tubes (TWTs) for a variety of satellite applications. These TWTs commonly employ an encapsulant in the region of the collector to function as an electrical insulator primarily, and often secondarily as a thermal conductor. The encapsulant material is generally polymeric in nature.

Polymeric encapsulants for electrical and electronic components can be useful and effective in providing electrical and thermal insulation only insofar as: (1) the encapsulant retains its chemical and mechanical integrity, and (2) it maintains a strong adhesive bond to its substrate. These characteristics of a polymer depend, in part, on its stability in the particular environment with respect to chemical change and evolution of gases or volatiles.

Specifically, for traveling-wave tubes (TWTs) in the region of the collector, a possible failure mode involving corona discharge has been identified as being due to gas evolution. Evolution of gas may be due to thermal degradation or to simple outgassing. In either case, gas evolution may: (1) provide a medium for corona discharge, (2) be a source of the hydrogen which has occasionally been detected within TWTs, or (3) adversely influence the mechanical properties of the encapsulant. Between the two possible mechanisms, thermal degradation would adversely influence the properties and performance of the encapsulant to a far greater extent than simple outgassing.

Initially, W-J had proposed to use RTV-11 (a General Electric Co. silicone polymer) as the encapsulant for this application. RTV-11 is known, however, to be a dirty system in the sense that it outgasses excessively and

*3333 Hillview Avenue, Stanford Industrial Park, Palo Alto, California 94304.

fails to meet vacuum condensable materials (VCM) requirements for use in space systems. Several sources made this known to W-J. Based in part on this information, W-J then proposed to use a polyurethane encapsulant, specifically Solithane 113.*

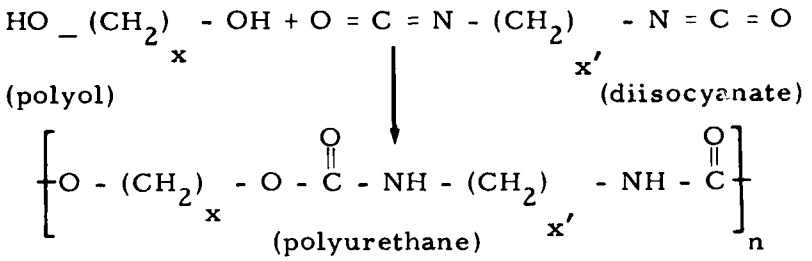
Since the Materials Sciences Laboratory was aware of the usual limitations in the thermal capability of polyurethanes in general, an investigation into the particular thermal stability of Solithane 113 was undertaken to verify its suitability for this application. This report describes that investigation using thermogravimetry and mass spectrometry under conditions approximating the most severe expected operating environment. Thermal degradation of Solithane was identified under these conditions, and the material is therefore considered inappropriate for this use.

*Solithane, Urethane Prepolymer, Thiokol Chemical Division, Thiokol Corporation, Bulletin TD-950, dated April 1976.

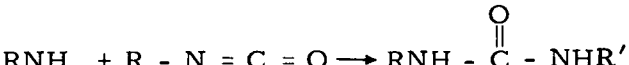
II. DISCUSSION

A. MATERIAL

Solithane 113 is a liquid urethane prepolymer cured by reaction with the polyol C113-300 and with triisopropylamine (TC-700). The generalized reactions may be depicted as follows:



(1)



(2)

In the particular formula supplied (No. 10), the proportions of prepolymer and curing agents were the following:

	Parts by Weight
Solithane 113 (Resin)	100.0
C113-300 (Polyol)	51.0
TC-700 (Amine)	4.5

The material was applied as a coating on an alumina tube ~1 in. o.d. × 1.5 in. long. The coating was then cured in air atmosphere at 150°F for 16 hours. It was supplied in this condition for evaluation.

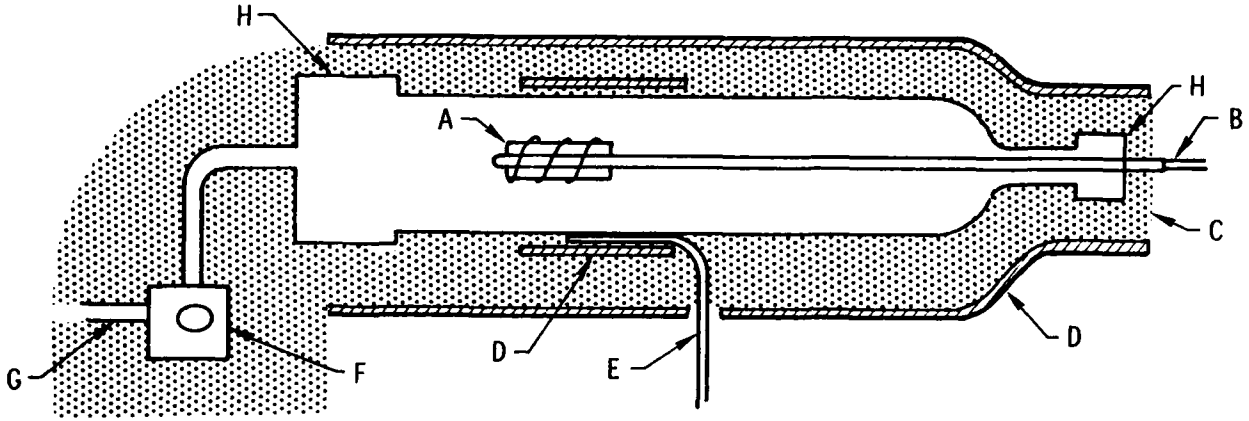
B. EXPERIMENTAL DETAILS

The specimens were prepared by dry cutting the ceramic tube with the attached polymer using a wire saw. Samples about 1/8 in. × 1/4 in. were used for the experiments.

Four specimens were placed in the aging apparatus (Figure 1). The chamber consisted of a Pyrex tube 5.0 in. × 0.75 in. i.d. with graded seals to Kovar tubulation on each end for attachment of standard stainless steel vacuum-tight fittings. After connection to a bakeable leak valve, an external thermocouple was added, held in place and insulated with Pyrex tape, and the tube was wrapped with heater tape. The internal thermocouple was used to monitor sample temperature continuously by means of a strip chart recorder. The external thermocouple was used to regulate temperature by feedback to a controller. The leak valve was attached to the inlet part of a quadrupole mass spectrometer and to an ion gauge.

Prior to aging the samples, the leak valve was opened and the samples and chamber conditioned by baking overnight under vacuum at 50°C. Ultimate system pressure during and after bakeout was 1.1×10^{-7} torr. Following bakeout, the leak valve was closed, and the internal chamber temperature was raised to 121°C (250°F). This temperature, ±5°C, was maintained without interruption during 312 hours (13 days).

Following this extended exposure, the gas content of the chamber was analyzed by bleeding the chamber atmosphere through the leak valve to the mass spectrometer. At this time, the system background consisted almost exclusively of CO, N_2, and O_2 at 1.2×10^{-7} torr (cf Figure 2). With the sample gases bleeding to the mass spectrometer to a pressure of 3.2×10^{-7} torr, significant increases were detected in the amounts of CH_4 and H_2O and large increases in mass-to-charge ratio (m/e) 28 and 44 (Figure 3). It should be noted that the quadrupole is a low resolution spectrometer that does not discriminate small differences in m/e; therefore, a detailed analysis poses major difficulties. Nevertheless, a partial interpretation of the composition



A	Sample	F	Variable Leak Valve
B	Thermocouple to Recorder	G	Sampling Line to Quadrupole Mass Spectrometer and Ion Gauge
C	Heater Tape		
D	Pyrex Tape		
E	Thermocouple to Controller	H	Vacuum Fittings

not to scale

Figure 1. Schematic of Experimental Apparatus for Polymer Thermal Stability Study (Not to Scale)

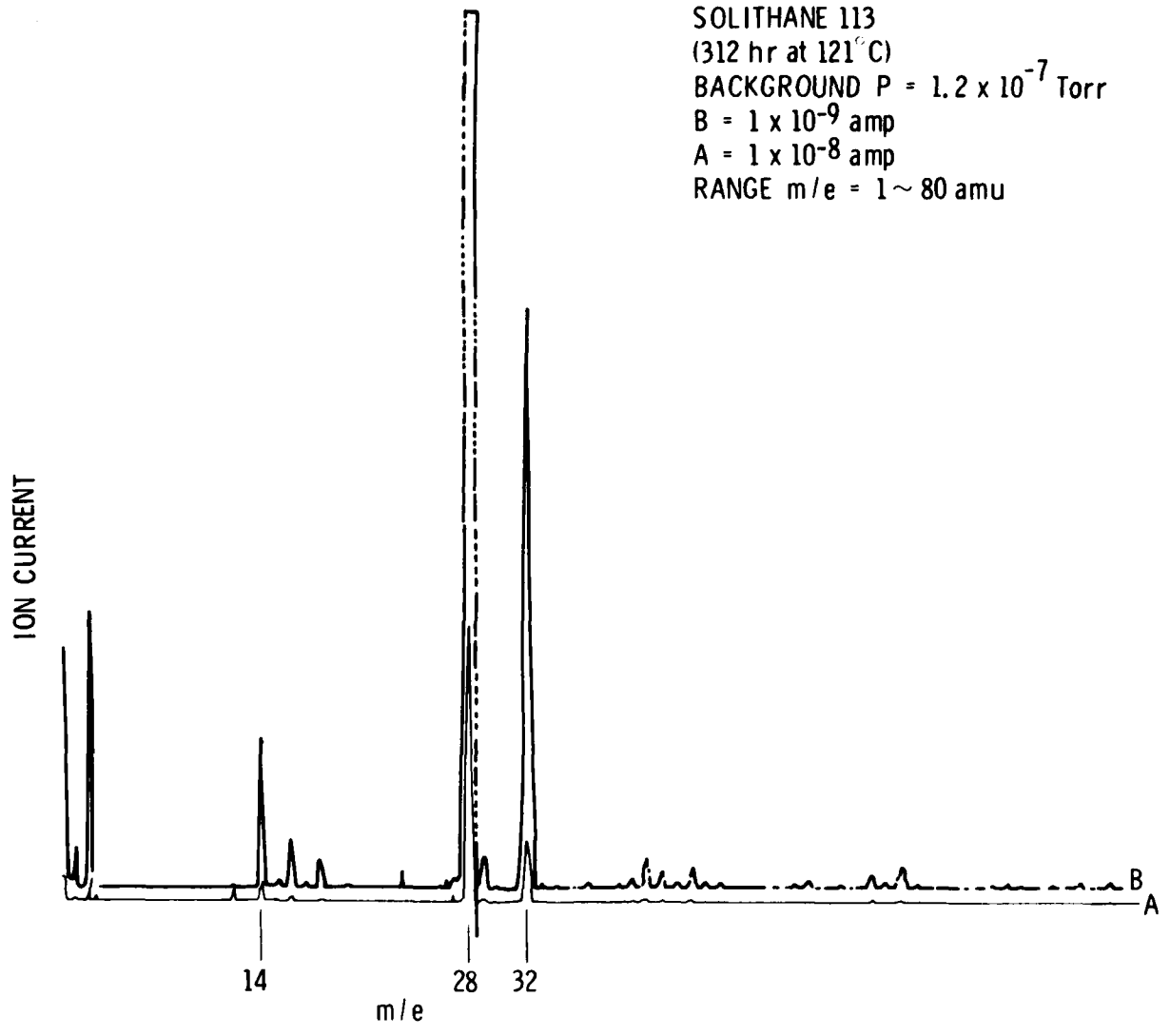


Figure 2. Quadrupole Mass Spectrometer System Background

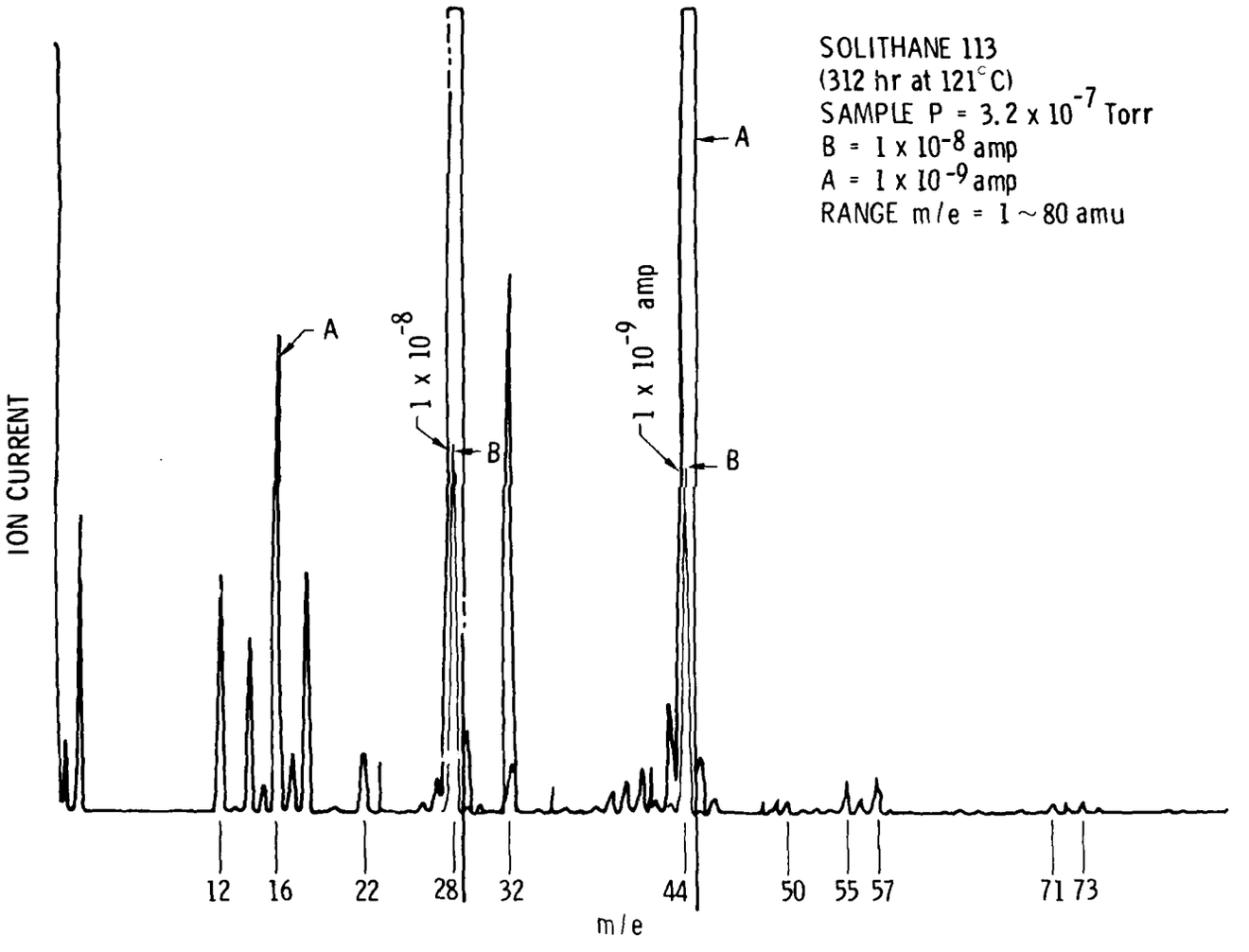


Figure 3. Spectrum of Gases and Vapors Evolved From Aged Solithane 113

of m/e 44 is possible. The interpretation is as follows: The presence of m/e 22 suggests doubly ionized CO_2^{++}; therefore, a large part of 44 can be attributed to CO_2. Fragments at 43 and 45 are probably related to oxygenated or nitrogenated aliphatic fragments; therefore, a mass 44 corresponding to $C_2H_6N^+$ and/or $C_2H_4O^+$ may be inferred. These latter two cannot be resolved by this method.

Reference to Reaction (1) on Page 4 shows an abundance of carboxyl ($C{=}O$ - O -) linkages that are a likely source of CO_2. Similarly, numerous $-CH_2$ - O - and $-CH_2$ - N = linkages would account for the oxygenated and nitrogenated fragments observed, assuming thermal degradation had occurred. There is also an increase in m/e 28 without a corresponding increase in m/e 14. This precludes the presence of nitrogen as a source of m/e 28, and the most reasonable interpretation is that the increase in this peak is due to evolution of CO. At the modest temperature of the experiments, the presence of CH_4 is unexpected, but its occurrence is unambiguous. The overwhelming thrust of the evidence is that significant thermal degradation has occurred.

In addition to the mass spectrometry, a thermogravimetric analysis (TGA) curve was run in air atmosphere at a heating rate of 1°C/min. Under these conditions, the onset of degradation occurs only at 175°C (cf Figure 4). This shows that such short-time exposures are insensitive to the effects of interest in this study.

A subsequent TGA in vacuum (Figure 5) was apparently more responsive to the behavior of the material. The onset of weight loss under these conditions is detected at about 50°C. The curve rapidly progresses to precipitous weight loss at fairly modest temperatures, suggesting catastrophic decomposition. Under isothermal (constant temperature) conditions (Figure 6) in air at 120°C, a situation that more nearly represents conditions of tube operation, weight loss is detected almost from the start of heating. Throughout the time period of exposure (to 80 hours), weight loss approximates a constant rate. All the above observations are consistent with an interpretation based on thermal degradation.

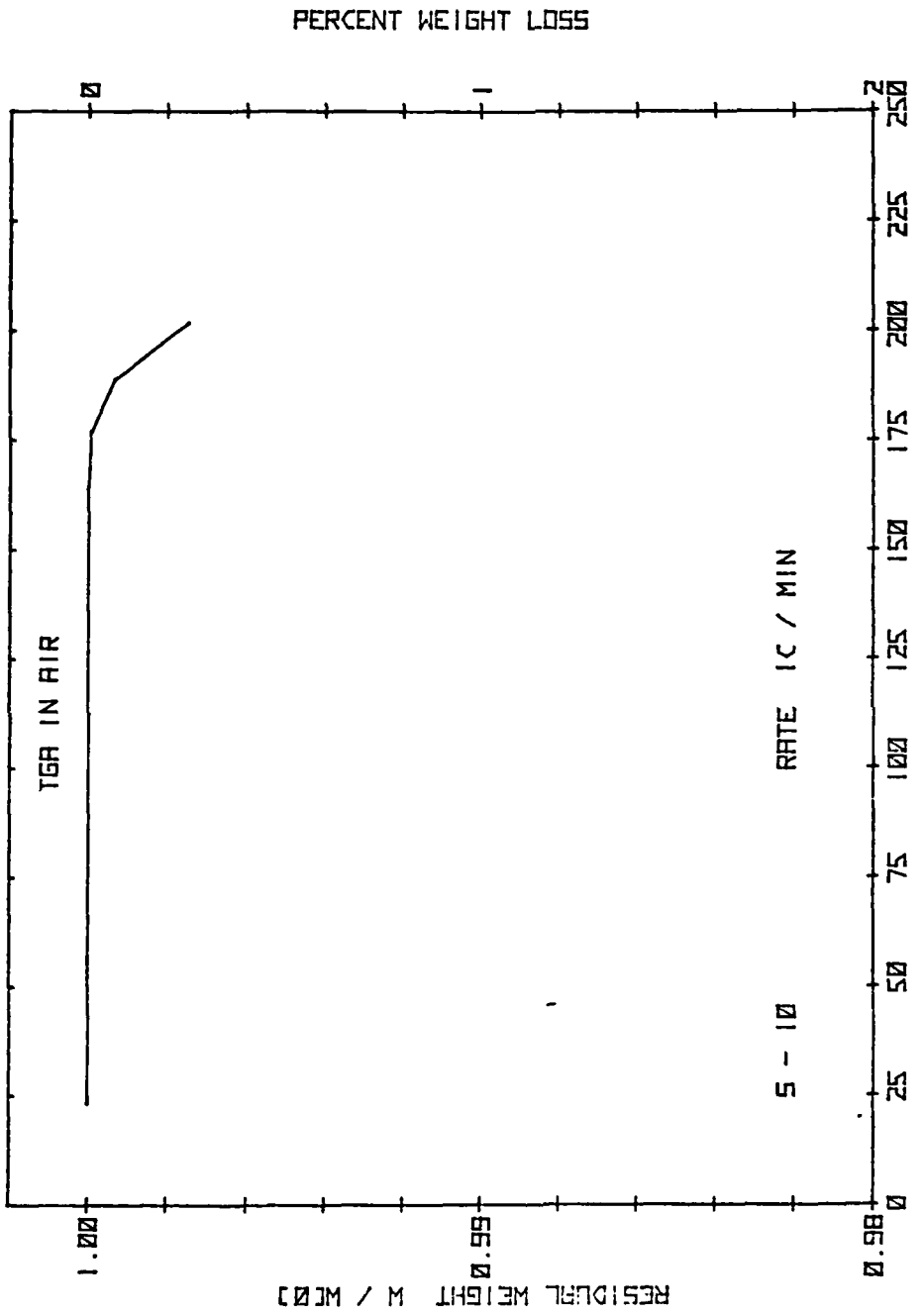


Figure 4. Solithane 113 TGA Curve in Air

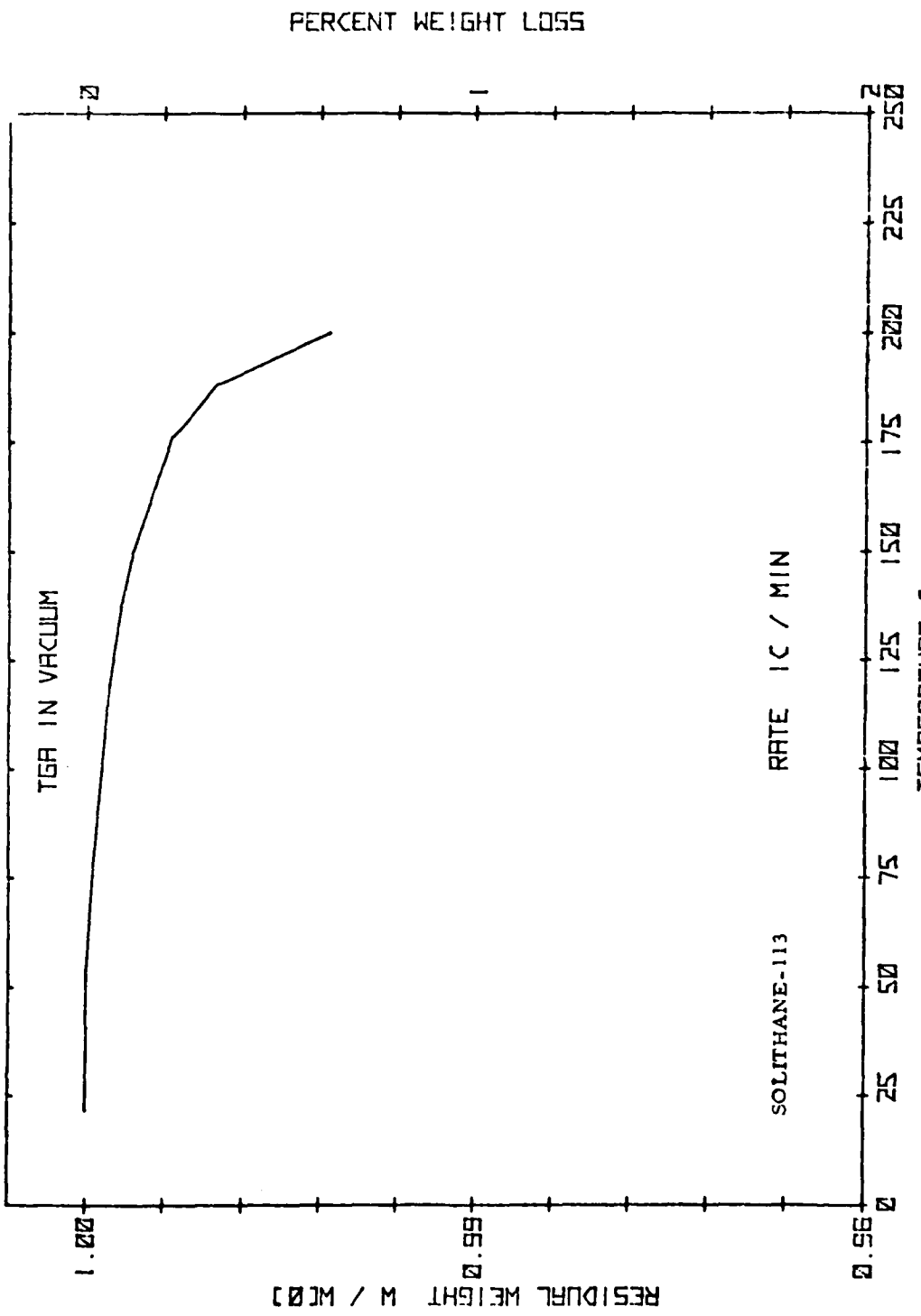


Figure 5. Programmed TGA of Solithane 113 in Vacuum

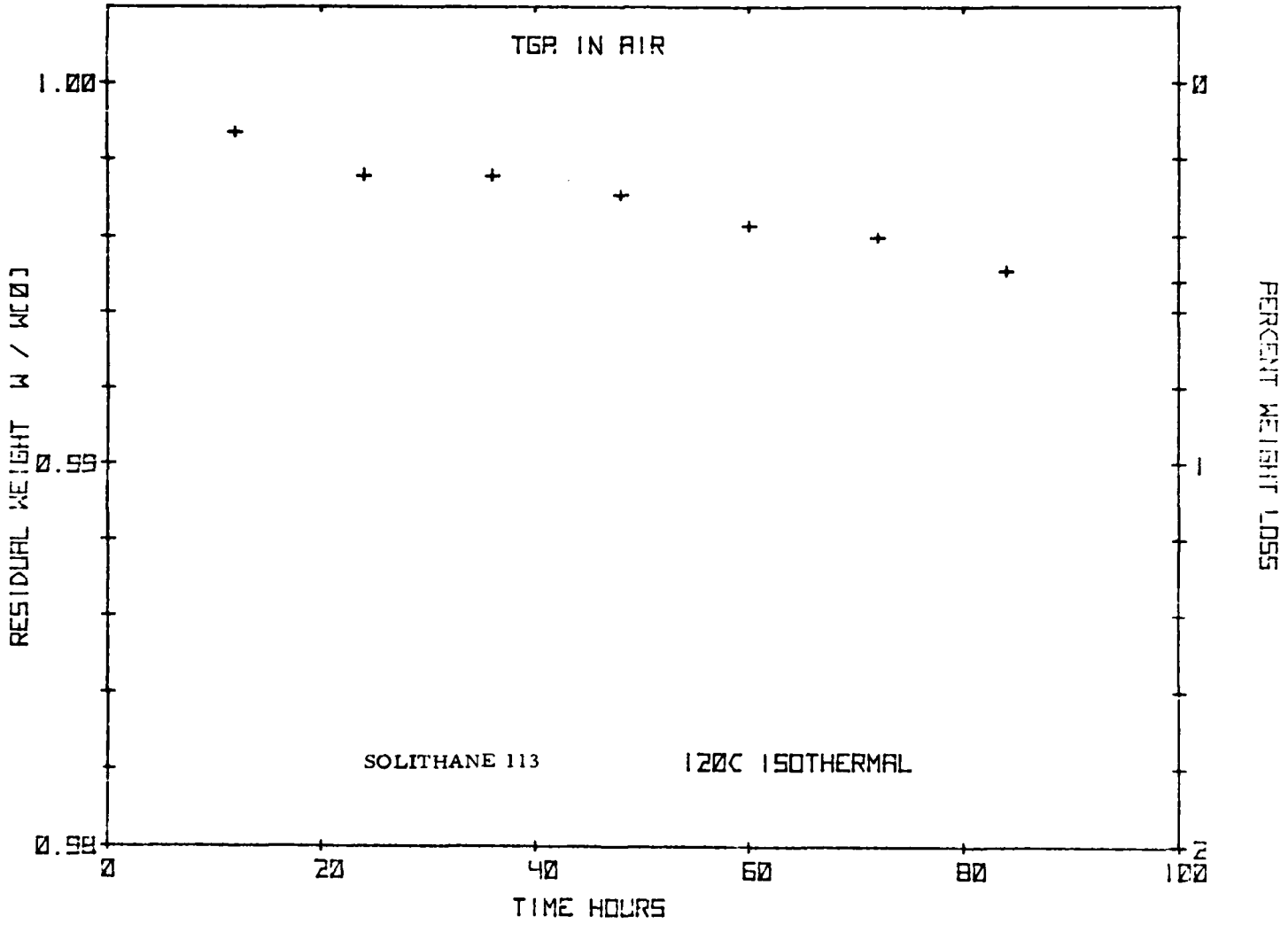


Figure 6. Isothermal TGA of Solithane 113 at 120°C in Air

III. CONCLUSIONS

These strictly qualitative experiments show that measurable thermal degradation occurs in Solithane 113 at 121°C ± 5°C in 13 days (312 hours) in a vacuum environment. The extent of this degradation is surprising in view of the manufacturer's available literature*. Nevertheless, continuing exposure to this environment, or long-term cycling to the temperature studied, may be expected to lead to significant degradation of the physical and chemical properties of the polymer. In selecting encapsulant materials for TWTA components, these effects need to be considered. They, in fact, raise the specter of potential tube failure by corona discharge occasioned by simultaneous mechanical degradation and evolution of gases.

*Solithane, Urethane Prepolymer, Thiokol Chemical Division, Thiokol Corporation, Bulletin TD-950, dated April 1976.